Preface

The transition metal perovskite oxides are a class of compounds that have been studied extensively for several decades due to their interesting structure-property correlations. Though they have been known for a long time, the discovery of high T_c superconductivity in cuprates and that of colossal magnetoresistance in manganites have brought them back to frontier research One of the most important areas of research involving transition metal perovskite oxides is the transition from metallic to insulating behaviour as a function of composition, temperature or pressure We have in this thesis studied the electrical transport properties of some of the perovskite related oxides thin films. The pulsed laser deposition technique is used to grow thin films of the transition metal oxides The growth of nearly single crystal like films on substrates like $LaAlO_3$ (100), $SrTiO_3$ (100) enabled us to study the highly correlated nature of the electrons in these oxide systems in the absence of any structural transformation

In the first chapter a brief introduction to the pulsed laser deposition process is given followed by an overview of transition metal perovskite oxides exhibiting various interesting properties We have also discussed the various known models that account for the conduction mechanism of these materials A brief introduction to each of the systems studied is given in the respective chapters. In chapter 2, the experimental techniques used for the investigation are given in details. While polycrystalline single-phase compounds are generally taken as the target to grow these films, sintered homogeneous mixtures

containing precursors with the right stoichiometry of metal ions is employed as the target to grow stoichiometric oxide films in this study.

We have chosen to study in our work four different types of compounds, which include typical metallic oxides to insulators and those exhibiting a transition from metal to insulator. The systems chosen are Na_xWO_3, K_xWO_3; $SrMoO_3$, $SrMoO_{3-x}N_x$; $LaVO_3$, $La_{1-x}Sr_xVO_3$ and $LaNi_{1-x}Mn_xO_3$, $LaNi_{1-x}Co_xO_3$, $La_{1-x}Ce_xNiO_3$. In chapter 3, we describe the fabrication of $SrMoO_3$ thin films by a unique method of fabrication involving the reduction of the target material in the laser plume by a reducing gas like hydrogen or ammonia. The use of ammonia resulted in the formation of $SrMoO_{3-x}N_x$ thin films. The strain due to the substrate is shown to influence the transport properties of the thin films. The thickness of the films and the substrate used is varied to understand the effect of strain on their conduction mechanism. A non-linear dependence of resistivity on temperature ($\rho \propto T^n$; n = 1.3 -1.42) is observed for these films throughout the temperature range (10-300 K) measured.

The details of the fabrication of sodium and potassium tungsten bronzes thin films are given in chapter 4. Na_xWO_3 thin films are shown to exhibit a metal to insulator transition for $x < 0.2$. The theoretical studies have predicted a critical concentration of $x = 0.18$ for the transition. Our study is in good agreement with the theoretical predictions. At low temperatures Na_xWO_3 metallic films show T^2 dependence. The conduction mechanism of the bronzes for various compositions and at different temperatures is also given. The highly crystalline films of K_xWO_3 deposited shows anomalous transport properties (metal-semiconductor-metal transition) owing to the stiffness of the lattices and also due to the electronic stability inherent in the system. The potassium tungsten

bronzes crystallize in hexagonal symmetry. The influence of the electron-electron and electron-phonon interactions present in the system on their conduction mechanism is also looked at.

The first-order structural transformation present in $LaVO_3$ and $La_{1-x}Sr_xVO_3$ systems at low concentrations of Sr is suppressed in the thin films as shown in chapter 5 The absolute value of resistivity shows prominent changes with the change in dopant concentration. The conductivity pattern also changes with change in composition for this Mott-Hubbard insulator. For metallic samples a nonlinear dependence of resistivity on temperature ($\rho \propto T^{1.5}$) is observed. For insulating compositions, at high temperatures an activated behaviour is observed while at low temperatures a variable range hopping mechanism is observed. The exponent of the equation, for compositions well in the insulating regime, shows signs of coulomb correlation The case is similar to that of Na_xWO_3 and in both these oxides the top of the valence band has mainly contributions from the d-band of the transition metal as seen from XPS.

In chapter 6, $LaNi_{1-x}Mn_xO_3$ and $LaNi_{1-x}Co_xO_3$ systems are described The films grow in the (100) direction with a pseudo cubic symmetry. The rhombohedral symmetry of the bulk samples has a cubic equivalent in the (100) direction At low temperatures a VRH mechanism is satisfied by Co doped systems but Mn doped system do not satisfy the conditions satisfactorily. While $LaNi_{1-x}Mn_xO_3$ system shows non-linear dependence on temperature for the intermediate ranges in the metallic regime, $LaNi_{1-x}Co_xO_3$ system shows linear behaviour of resistance throughout the temperature range measured. Mn and Co doped systems also exhibit colossal magneto resistance at low temperatures For all the nickelates fabricated, the high resistance films show small polaron conduction

mechanism at high temperatures. This is assumed to be related to the lattice polarization present in these systems that is associated with the reduction in Ni valency.

In chapter 7, we have shown the doping of Ce^{4+} ions in the La^{3+} site of $LaNiO_3$ perovskite. Even though bulk $La_{1-x}Ce_xNiO_3$ has not been synthesized by any synthetic method so far, we have grown films of Ce doped $LaNiO_3$. The fabrication in the form of thin films is believed to be possible due to the non-equilibrium conditions prevailing in the PLD technique As the cerium ion concentration is increased, there is an expansion of the lattice Above x = 0 2, there is a change in the symmetry of the lattice from rhombohedral to orthorhombic symmetry due to smaller Ce^{4+} ion substitution with simultaneous increase in Ni ionic size due to change in the oxidation state of Ni^{3+} to Ni^{2+} Above x = 0.6, the $La_{1-x}Ce_xNiO_3$ phase does not form La_2NiO_4, CeO_2 and NiO phases are seen clearly in the x-ray diffraction pattern Metal-insulator transition observed around x = 0.3 is associated with a structural transition from rhombohedral to orthorhombic structure with lattice parameter a ~ $\sqrt{2}a_0$ = 5.47 Å, b ~ $\sqrt{2}a_0$ = 5 47 Å and c = 7 94 Å.

In the last chapter, a critical review of the conduction mechanism observed in various systems studied here is described The value of minimum metallic conductivity observed in each of the above systems in the metal-insulator transition regime lie within the range 330-70 S cm^{-1}.